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Professor Stan Kolaczowski 10 Dec 2015

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Using quadrupole mass spectrometry for on-line gas analysis – gasification of biomass and refuse derived fuel

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ABSTRACT

A quantitative method of on-line gas analysis was developed, using quadrupole mass spectrometry to measure gas composition when charcoal, wood, straw, and refuse derived fuel were gasified. Despite overlapping between some of the species, the method was demonstrated on small-scale laboratory gasifiers, recording the main components (e.g. N₂ ~ 54-67 vol.%; H₂ ~ 5-13 vol.%; CO₂ ~ 15-17 vol.%; CO ~ 10-17 vol.%), and lower levels of CH₄ (~ 1-2 vol.%) and O₂ (~ 0.1-1 vol.%) in the gas. Trace levels of H₂S (~ 100-300 ppmv) and COS (~ 10-30 ppmv) were also measured (important for gas clean-up strategies). On-line measurements were performed on a commercial pilot-scale down-draft gasifier (using waste wood), and the concentrations of H₂S varied from 200 to 700 ppmv, and COS from 7 to 17 ppmv. The ratio of H₂S: COS was higher than in the laboratory trials - probably because of COS hydrolysis reactions taking place in the wet scrubbing systems.

Key words: Biomass gasification; gasifier; down-draft; on-line gas analysis; quadrupole mass spectrometry (QMS).

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24 **1. Introduction**

25

26 Because the supply of oil and natural gas resources is finite, biomass is
27 considered as a potential feedstock for the supply of energy and chemicals in the future.

28 There are three main ways to convert biomass into energy, namely: pyrolysis,
29 combustion and gasification, in which pyrolysis and gasification technologies are
30 attractive, as the gas produced (producer gas) is in a suitable form for either energy
31 conversion or as a chemical feedstock [1]. The pyrolysis process generally produces
32 three products (gas, bio-oil, and char), whereas in the gasification process, biomass is
33 almost completely converted into gaseous products (except for the ash in the feed).
34 Therefore, biomass gasification is considered to be an important technology to supply
35 cleaner gases for many end-use applications such as combined heat and power using a
36 gas engine or fuel cells, and in chemical synthesis.

37 Depending on the way in which the gas is used [2], different restrictions apply
38 on the concentrations of the contaminants in the gas produced. In addition, final
39 emissions from the plant need to conform to environmental regulations that apply where

List of Abbreviations

GC	Gas Chromatography
HESS	High Efficiency Water Scrubber
IR	Infrared
NDIR	Non-Dispersive Infrared Analyzer
QMS	Quadrupole Mass Spectrometry
RDF	Refuse Derived Fuel
RS	Relative Sensitivity
SEM	Secondary Electron Multiplier
TCD	Thermal Conductivity Detector

40 the plant is operated. For example, in Europe, if a refuse derived fuel is used, then the
41 Waste Incineration Directive [3] applies, and in such a situation in order to design the
42 gas clean-up system, it is important to know the concentration of contaminants such as
43 H₂S and COS [4]. Thus, the ability to perform on-line analysis is beneficial for
44 monitoring the quality of the gas produced, both at an industrial and an experimental
45 scale of operation.

46 To analyze the gas produced from a biomass gasification system, discrete samples of
47 gas may be taken and then analyzed by a specialist laboratory. Such analysis can be
48 done using gas chromatography (GC), or with an infrared (IR) system, and these two
49 methods of measurement are often used. The main advantage of GC is that it can
50 provide a quantitative analysis of complex gas mixtures, whereas its main drawback is
51 the long measuring time. Therefore, it is not a suitable method for on-line analysis
52 during transient operating conditions encountered in a gasification process. Also, even if
53 a set of discrete samples were to be taken for subsequent analysis, then problems can
54 often be encountered either, with possible leakage of species (e.g. hydrogen) from the
55 sample container, or difficulties in the sampling process, both resulting in incorrect
56 results.

57 Although IR spectroscopy could be used to perform measurements on-line, its main
58 disadvantage arises from the fact that, in general, it measures a single gas species, and
59 hence information on the other key components in the gas mixture is missing. It is
60 therefore not unusual to find in the literature that a combination of GC and IR
61 techniques is used. For example, Craig [5] reports the use of both methods, using a non-
62 dispersive infrared analyzer (NDIR) to monitor continuously levels of CO and CO₂.
63 The concentrations of the other gases e.g. H₂, CH₄, NO_x, O₂ were obtained from

64 measurements on samples taken every 15 minutes, and the GC was one of the analytical
65 instruments used. Ntshengedzeni and Edson [6] used an NDIR technique to measure the
66 composition of the gas produced from an Imbert downdraft gasifier. However, only five
67 gases were analyzed (CO , H_2 , CO_2 , CH_4 , N_2), providing information on gas
68 composition at one minute intervals.

69

70 In the literature, there is evidence of an interest (and hence need) to perform on-
71 line analysis of the gas produced. Examples include work done by Karellas and Karl [7],
72 where the producer gas stream from a fluidized-bed gasifier was analyzed on-line by
73 means of laser spectroscopy; however, only the concentrations of the main constituents
74 (H_2 , CH_4 , CO , CO_2 , H_2O) and some heavier hydrocarbons were reported. In Karlegård
75 *et al.* [8], the use of quadrupole mass spectrometry (QMS) for on-line analysis of gas
76 (from gasification process) was reported. Nevertheless, this method was limited due to
77 its complexity, and it was only tested for a very narrow range of concentrations of
78 species in the gas.

79 Although QMS is already used in many industries, its use for the analysis of fuel
80 gas streams is not so widespread [8, 9]. In addition, despite being a well-established
81 technique, there are still some technical difficulties in using it for the on-line analysis of
82 multi-component gas mixtures. For example, Turner *et al.* [10] reported that the
83 accuracy of measurements using QMS was questionable due to the non-linearity and
84 instability of this method. Furthermore, overlapping fragments at similar m/z values can
85 make the identification of individual species difficult.

86 In this paper, a methodology is developed to illustrate how QMS may be used
87 for on-line analysis of gas species. There were challenges that had to be overcome, as

there were overlaps in the signals from some of the species (e.g. N₂ with CO), and the magnitude of the concentration of the species also varied. The technique is developed and illustrated by first performing some measurements on a relatively clean gas (from the gasification of charcoal with steam), and then on a more challenging system when wood, straw and refuse derived fuel (RDF) pellets are gasified (partial oxidation with air) in a laboratory-scale gasifier. Finally, it is applied to measure in real-time, the composition of the gas produced from a commercial pilot-scale plant, using waste-wood as a fuel.

2. Material and methods

2.1. Gas chromatography

To help validate the measurements using QMS, measurements were also performed using gas chromatography (GC).

This method is often used for quantitative analysis even of very complex gas mixtures. However, its main drawback is the time it takes to obtain a measurement, as this depends on the retention time in the column. If real-time analysis is required (e.g. to follow a transient), then this method is unsuitable. The gas chromatograph used was a Chrompack CP9001, fitted with one pre-column and one molecular sieve column (connected in series), and a thermal conductivity detector. The chromatograph was calibrated using calibration gas mixtures with argon as the carrier gas.

To check the repeatability of measurements using GC, a bag-sample of gas was taken during a steam gasification of char experiment, which was run at 800 °C over a

112 period of 45 minutes. To this bag a quantity of air was added from a gas cylinder, so
113 that O₂ was also present. The gas was then injected into the column 10 times, and the
114 average gas composition (vol.%) was: H₂ = 28.68 (± 0.56); CO₂ = 7.60 (± 0.50); O₂ =
115 7.51 (± 0.35); N₂ = 48.01 (± 0.73); CO = 7.79 (± 0.82); CH₄ = 0.56 (± 0.09).

116

117 ***2.2. Quadrupole mass spectrometry (QMS)***

118

119 Mass spectrometry identifies the species by using the difference in mass-to-
120 charge ratio (m/z) of ionized atoms or molecules. It is very useful to quantify atoms or
121 molecules, and to determine chemical and structural information about molecules. Each
122 molecule has its own distinctive fragmentation patterns that help to identify its structure.
123 Further information can be found in the literature [11]. In this study, a standard Hiden
124 HPR-20 Quadrupole Mass Spectrometer was used, which made use of Hiden's MASsoft
125 software. This enables data to be reviewed, and it had export facilities that were
126 compatible with the Windows™ operating systems.

127

128 ***2.2.1. Setting the operating parameters***

129 Before a methodology can be developed, the operating parameters for QMS
130 need to be set. The resolution and sensitivity of QMS depends on these conditions. After
131 calibration, any changes in these parameters will result in adverse effects on
132 repeatability [10].

133 **Detector selection:** Either a Faraday cup, or an Electron multiplier (SEM
134 detector) may be selected depending on the concentrations of the species in the gas. To
135 detect a trace level of gas, an SEM detector with a detectable pressure range from 1×10⁻

136 ⁷ to 1×10^{-13} torr (1.3332×10^{-10} to 1.3332×10^{-16} bar) could be selected, whereas, the
137 Faraday detector would be more suitable for a gas with a detectable pressure range from
138 1×10^{-5} to 1×10^{-10} torr (1.3332×10^{-8} to 1.3332×10^{-13} bar) [12].

139 In preliminary experiments, it was found that the selection of a suitable detector
140 (or a combination of both SEM and Faraday) for a particular gas mixture affects not
141 only the sensitivities, but also the measuring time. If the SEM detector is selected, it is
142 necessary to calibrate the voltage applied so that it gives an equivalent signal to that of
143 the Faraday detector. This voltage value changes slightly depending on the mass number
144 and helps to increase the sensitivity when measuring trace levels of gases.

145 **Electron emission:** This maximizes the sensitivity for a particular gas. The
146 value of this parameter is selected for a particular gas mixture by using a calibration
147 facility in MASsoft, in which the highest concentration of gas in the mixture should
148 give approximately 1×10^{-5} torr (1.3332×10^{-8} bar) [12]. Above this value, the signal
149 becomes non-linear, leading to inaccurate results.

150 **Electron energy:** This is normally set at 70 eV [10], and this will singly and
151 doubly ionize most species. However, to minimize second ionization (producing a
152 signal at $\frac{1}{2}$ mass) electron energy can be adjusted to optimize the signal without double
153 ionization.

154 **Measuring time:** For on-line analysis, measuring time is important and depends
155 on a number of operating parameters such as: the detector used, acquisition range, dwell
156 and settle times. It was found that by reducing both the dwell and settle times, and also
157 narrowing the acquisition range, then this helped to increase the number of
158 measurements per minute. However, these values need to be optimized to avoid an
159 undue reduction in accuracy.

160 **Operating Pressure:** During experiments, it was noticed that any change in the
161 base pressure (the vacuum operating pressure), had a strong negative effect on the
162 accuracy of the measurement. This is consistent with findings in Turner *et al.* [10].
163 Thus, during an experiment, this operating pressure must be carefully monitored and
164 adjusted (by using the sample by-pass control valve).

165 **General operating procedure:** This is an important factor, and was also found
166 to affect the accuracy of the measurements (also discussed in Turner *et al.* [10]). In this
167 paper, both the Faraday and the SEM detectors were used to analyze gas mixtures
168 containing: N₂, CO, H₂, CO₂, CH₄, and trace gases of O₂, H₂S and COS. The values of:
169 SEM detector's voltage, electron emission, and electron energy, were all optimized and
170 set at: 910 V, 250 uA and 70 eV, respectively. The analysis frequency was up to 10
171 samples per minute, which was considered adequate for the planned set of experiments.

172 The mass spectrometer was started-up and left running for at least two days to
173 obtain ultimate base pressure and stability prior to measurement. Then, the filaments
174 were also switched on and left running for 24 hours (to warm-up) prior to measurement.
175 A final base pressure of 1.6×10^{-6} torr was achieved.

176
177
178 2.2.2. *Method development*

179 **Challenges:** Turner *et al.* [10] reported that mathematical methods are important
180 to provide both qualitative and quantitative information from mass spectra. Basically,
181 these methods are based on the assumption that the measured spectrum is linear for each
182 pure component [13, 14]. However, if the sample was a complex mixture, then
183 considerable errors were noted [8, 14]. In attempts to solve this problem, some other
184 methods have been developed [9, 14], in which normalization methods are frequently
185 employed.

186 When using QMS to measure a mixture consisting of different species, it is often
187 difficult to separate some of the species in the mixture due to spectral interference and
188 the extensive fragmentation of the ions produced [14], particularly for organic species,
189 which because of their characteristic have complex fragmentation patterns. In theory,
190 this problem may be solved by the selection of non-interfering peaks. However, in
191 practice, this is not always easy to do.

192 The gas stream to be analyzed may consist of H₂, CO, N₂, O₂, CO₂, CH₄, H₂O,
193 C₂ & C₃ hydrocarbons, argon, longer chain hydrocarbons such as tars, and other
194 contaminants such as sulphur and nitrogen compounds. In this study, a method was
195 developed to measure the concentrations of the main gases (H₂, CO, N₂, CO₂, CH₄) and
196 the trace gases (O₂, H₂S and COS) in a dried gas stream. In this case, three gases
197 consisting of N₂, CO and CO₂ exhibit similar fragmentation patterns in the mass spectra.
198 This can be problematic to even the experienced mass spectrometrists. Karlegård *et al.*
199 [8] also reported that the quantification of N₂ and CO in gas mixtures (biomass
200 gasification) was a problem for QMS analysis. According to Cook *et al.* [9], “in normal
201 operation, a Quadrupole Mass Spectrometer does not have sufficient resolution to
202 distinguish ‘isobars’ (ions of different elemental composition but the same nominal
203 mass; e.g., CO at 27.99491 Da and N₂ at 28.006 Da both have nominal mass ‘28’).”

204 It can be said that, for building an on-line analysis method using QMS, it is
205 beneficial to deal with as few mass fragments as possible. This helps to reduce the
206 complexity of the method, leading to an increase in the measuring time of
207 measurements. However, for a complex gas mixture, the use of more fragments could
208 improve the accuracy of measurements. For example, Karlegård *et al.* [8] failed in
209 analyzing the gas produced from gasification of biofuel when they selected mass

210 fragments of $m/z(12)$, $m/z(14)$, $m/z(28)$ and $m/z(44)$ to separate N_2 , CO and CO_2 . In that
211 study, the authors used an external method that attempted to determine absolute analyte
212 concentrations from absolute signal intensities. This method, according to Cook *et al.*
213 [9] and Hoffmann and Stroobant [14], is considered not to give good measurement
214 repeatability due to the difficulty of controlling operating parameters, such as electron
215 emission from the hot filament, in a precise manner.

216 Therefore, in the present study, with the aim of improving the speed and
217 accuracy of the analysis method, fewer mass fragments would be used. Normalizing to
218 the total ion current (estimated by summing the peaks) was selected to build the method.
219 This method (called internal standard) is based on a comparison of the intensities of the
220 signal, corresponding to the product that has to be quantified, with the signal of a
221 reference compound. It provides the smallest sum of the squares of the difference
222 between the calculated and experimentally measured mixture spectra – this is known as
223 least-squares analysis [9].

224 **Building the method:** In order to quantify the individual components in the gas
225 mixtures (from the experiments), the method consisted of:

- 226 ▪ The identification of all molecular ions / significant peaks.
- 227 ▪ The identification of peaks due to known components.
- 228 ▪ The assignment of remaining peaks noting the general appearance of the
229 spectrum, checking for peak clusters from isotope patterns and low-mass
230 neutral fragment loss.
- 231 ▪ The comparison of results with reference spectra on the database [13].

232 Then, a number of spectra were selected to create the mathematical method for
233 quantification. Table 1 shows the mass fragments used in the analysis.

234 In general, the ion-molecule fragment of a species is often chosen, as it is the
 235 most intensive signal (the base peak) compared to the other spectra. However, for CH₄,
 236 because there is an overlap with oxygen at a value of m/z(16), the spectra of CH₄ at
 237 m/z(15) was selected.

238 For H₂, CH₄, and CO₂, the values obtained did not need to be corrected. The
 239 partial pressures of H₂, CH₄ and CO₂ were derived from peaks corresponding to values
 240 at m/z(2), m/z(15) and m/z(44), respectively. Therefore:

$$241 \quad \begin{cases} P_{H_2} = P_{m/z(2)} \\ P_{CH_4} = P_{m/z(15)} \\ P_{CO_2} = P_{m/z(44)} \end{cases} \quad (1)$$

242 where: P_i and $P_{m/z(j)}$ are the corrected partial pressure of component i, and the raw partial
 243 pressure recorded by the QMS at peak m/z(j), respectively.

244 For N₂ and CO, because there are overlaps with some of the species:

- 245 ■ the partial pressure of N₂ was derived from the m/z(14) N₂ spectra, which
 246 was corrected for CH₄, and also CO overlaps (possibly from a second
 247 ionization peak at ½ mass), while
- 248 ■ that of CO was derived from the m/z(28) peak, corrected for N₂ and CO₂
 249 overlaps.

250 The following two equations were applied to separate N₂ and CO, and these
 251 featured in the iterative mathematical method used.

252 The partial pressure of N₂, after being corrected for CH₄ and CO overlaps:

$$253 \quad P_{N_2} = P_{m/z(14)} - P_{CH_4} \frac{C_{CH_4(14)}}{C_{CH_4(15)}} - P_{CO} \times C_{CO(14)} \quad (2)$$

254 The partial pressure of CO, after being corrected for N₂ and CO₂ overlaps:

$$P_{CO} = P_{m/z(28)} - P_{N_2} \times \frac{1}{C_{N_2(14)}} - P_{CO_2} \times C_{CO_2(28)} \quad (3)$$

where: $C_{i(j)}$ is the ratio of partial pressure of component i, at peak m/z(j) to that of component i, at the main peak (the highest peak of component i), and can be collected from the software's library. However, these ratios change, depending on the operating parameters. Thus, in this study, they were calculated from a calibration at operating conditions.

For the species, H₂S and COS, very careful checks were performed to avoid spectral interference with other species (e.g. main gases, tars, and other contaminants). Thus, the non-interfering peak of m/z(60) was chosen for COS, whereas H₂S partial pressure was derived from the m/z(34) peak, corrected for O₂ overlap. Similarly, partial pressure of O₂ was derived from the m/z(32) peak, corrected for H₂S overlap.

The partial pressure of COS:

$$P_{COS} = P_{m/z(60)} \quad (4)$$

The partial pressure of H₂S, after being corrected for O₂ overlap:

$$P_{H_2S} = P_{m/z(34)} - P_{O_2} \times C_{O_2(34)} \quad (5)$$

The partial pressure of O₂, after being corrected for H₂S overlap:

$$P_{O_2} = P_{m/z(32)} - P_{H_2S} \times C_{H_2S(32)} \quad (6)$$

Finally, the concentrations of the species were calculated from:

$$x_i = \frac{(P_i / RS_i)}{\sum_i (P_i / RS_i)} \quad (7)$$

where: x_i and RS_i are the calculated concentration and relative sensitivity (RS value) of component i, respectively.

277 2.2.3. Calibration

278 To quantify the gases in a mixture, it is necessary to calibrate for RS values. RS
279 is a factor which takes into account the sensitivity of different species dependent on the
280 efficiency of the quadrupole. It is best to determine these for the specific quadrupole
281 mass spectrometer used, at its particular set of operating conditions. The calibration
282 requires a known gas mixture, and the highest concentration of gas is assigned a
283 sensitivity of 1 (in this study, N₂ was selected and became the reference gas).

$$284 \quad RS_i = \frac{P_i}{P_{N_2}} \times \frac{x_{N_2}}{x_i} \quad (8)$$

285 where: x_{N_2} and x_i are the known concentrations of reference gas N₂ and component i,
286 respectively.

287 The gas mixture used to test the gas chromatograph (see Section 2.1), was then
288 used to calibrate the mass spectrometer, for the main components in the gas. For the
289 trace gases, the RS values of H₂S and COS with N₂ as the reference gas were calculated
290 by calibration with 2000 ppmv H₂S in N₂, and 200 ppmv COS in N₂.

291

292 2.3. Experimental

293

294 2.3.1. Laboratory-scale gasifier

295 Gasification experiments were performed in a small laboratory-scale quartz-tube
296 gasifier, in which in earlier work [15], it was shown that it can produce a gas stream
297 similar in composition to a pilot-scale gasifier. An outline schematic of the gas sampling
298 scheme is shown in Figure 1.

299 The gas flowed from the bottom of the gasifier, then through a cooler, and any
300 condensate was trapped in the first plastic vessel. The gas then passed through a cooling
301 coil, where more of the liquid was condensed. The gas was then passed through a glass
302 wool filter, and then discharged into the vent from the fume cupboard. Samples of gas
303 were drawn from the exhaust line, and passed through another glass wool filter and a
304 filter coalescer before going to a gas chromatograph and the mass spectrometer for
305 analysis. This system of filters helped to remove the majority of tars and particulates in
306 the gas stream (so as not to damage the analytical equipment). Further details on this
307 experimental set-up are available in earlier work [15].

308

309 2.3.2. *Measurements on a pilot-scale plant*

310 Gas analysis measurements were also taken on a commercial pilot-scale plant
311 operated by Refgas Ltd at a test site in Sandycroft (near Chester, UK). A ‘waste-wood’
312 was used as a fuel. The term ‘waste-wood’ is used to describe a material that has been
313 mainly produced from recycled wood, but may also contain a small amount of other
314 contaminants (e.g. plastic, paper).

315 In its present configuration, this pilot-plant had a nominal capacity of 150 to 250
316 kg/h, depending on the material fed into the gasifier and the choice of operating
317 conditions. The potential electrical output from the gas produced from this plant could
318 vary from 150 to 250 kW_e.

319 A simplified schematic of the process flow diagram is shown in Figure 2.
320 The waste-wood chips were fed from a hopper into the gasifier. The down-draft gasifier
321 operates under a negative pressure, and the gases are drawn from the gasifier by the
322 centrifugal gas blower. Because of the negative pressure in the gasifier, air is drawn into

323 the gasifier, and this supports the combustion and partial oxidation reactions that take
324 place inside this unit. Some of this air is preheated in the outer jacket around the two
325 cyclones. Another quantity of air is fed at ambient temperature directly into the gasifier
326 along the central shaft.

327 The gas leaves the reactor at the bottom of the unit, at a temperature of about
328 550 °C. Char is discharged from the base of the gasifier, and char fines/ash are also
329 trapped in the two cyclones. The dirty gas from the cyclones is quenched with water,
330 and then passes through a HESS unit (which is a high efficiency water scrubber). The
331 gas then passes through a heat exchanger (chiller), where additional residual water/tars
332 are condensed. The blower draws the gas from the gasifier, and then blows it (under
333 positive pressure) through the filters, into the storage tank, and then to the gas engine,
334 and/or to the gas flare. The gas engine has the capacity to produce electrical energy.
335 During the course of measurements on the plant, the gas was discharged to flare.

336 The gas sample to the mass spectrometer was drawn from the line, at the point
337 where the gas was sent to flare (see Figure 2). At this point, the gas was at positive
338 pressure. The gas sample then flowed through a glass wool filter and a filter coalescer,
339 (same procedure as shown in Figure 1), before going to the mass spectrometer for
340 analysis.

341

342 **3. Results and discussion**

343

344 ***3.1. Experiments in laboratory-scale gasifier***

345

346 A series of experiments was performed to generate gases that had different
347 compositions, but at the same time reflected compositions which could be encountered
348 in real applications.

349 *3.1.1. Proximate analysis of fuels*

350 Table 2 shows the proximate analysis of fuels used for the gasification
351 experiments that were done in the laboratory. Experiments were performed with
352 charcoal, wood, straw and refuse derived fuel (RDF) in the form of pellets.

353

354 *3.1.2. Reliability check of the developed QMS method*

355 A gas stream was generated by the use of a steam in nitrogen mixture to gasify
356 charcoal. The molar ratio $\text{H}_2\text{O}:\text{N}_2$ was 2:1, and N_2 and H_2O flows were 0.1 litre/min and
357 0.196 g/min, respectively, passing through a 9.5 mm i.d. tube reactor, packed with
358 charcoal (4 mm in diameter). The gas composition was measured on-line using QMS
359 over a period of 45 min, while the temperature of the furnace was gradually increased
360 from 600 to 900 °C, see Figure 3. At 5½ min intervals, gas samples were taken and
361 analyzed using GC equipped with a thermal conductivity detector (TCD). The data from
362 QMS is presented as a continuous curve (because measurements are frequent), and the
363 data using GC is in the form of discrete data points. From these results it is clear that:

- 364 - a very good match was obtained between QMS and GC,
365 - as the gas composition was measured over a wide range of concentrations
366 (which arose as a result of the experiment), the match between QMS and GC
367 remained very good. For example:

- 368 ▪ For N_2 in the range of 21 to 100 vol.% (it was within ± 2.1 % of the
369 value).

- 370 ▪ For H₂ in the range of 0 to 44 vol.% (it was within ± 2.7 % of the value).
- 371 ▪ For CO in the range of 1.2 to 29 vol.% (it was within ± 3.7 % of the
- 372 value).
- 373 ▪ For CO₂ in the range of 2 to 14 vol.% (it was within ± 2.1 % of the value).
- 374 ▪ For CH₄ in the range of 0.45 to 1 vol.% (it was within ± 12.7 % of the
- 375 value).

376 Big differences only occurred at low concentrations of CO, CO₂, and CH₄.

377 To check on the accuracy of the method for H₂S, COS, and O₂ detection, some
378 experiments were done using 2000 ppmv H₂S in N₂, 200 ppmv COS in N₂, and air,
379 respectively. These were tested in ‘as supplied form’, and they were also diluted with
380 nitrogen (using rotameters). The results show that there was a good match between the
381 measured values and those calculated from gas flows using rotameters (e.g. H₂S in the
382 range of 0 to 2000 ppmv (it was within ± 1.1 %); COS in the range of 0 to 200 ppmv (it
383 was within ± 2.0 %); and O₂ in the range of 0 to 21 vol.% (it was within ± 9.5 %)).

384 In general, these results were most satisfying, as the methodology was shown to
385 work and produce good results.

386

387 3.1.3. *The composition of the producer gas from gasification of wood pellets*

388 Having established that the QMS method worked well for a relatively clean gas,
389 a more complex gas mixture was used. This was produced by the gasification of wood
390 pellets (using partial oxidation). These experiments were performed in a small scale, 21
391 mm i.d. quartz tube gasifier filled with wood pellets (5 mm diameter, and 13 mm long),
392 to a depth of about 400 mm. The air flow was kept constant at 3 litre/min, and

temperatures in the hot zone were in the region of 912 to 1046 °C. Further information on that experimental facility is available in Kolaczowski *et al.* [15].

An example of measurements on dry gas is shown in Figure 4. In this example, the average trace gas concentrations were: O₂ = 1510 ppmv; H₂S = 99 ppmv, and COS = 10 ppmv.

To check the repeatability of measurements with QMS, a bag-sample of gas was taken during this wood gasification experiment. The gas was then connected to the sampling line to the mass spectrometer. The repeatability was checked over a 10-minute period, during which it was found that the average composition of the species was: N₂ = 58.34 (± 0.28) vol.%; CO = 15.62 (± 0.16) vol.%; H₂ = 9.1 (± 0.16) vol.%, CO₂ = 14.31 (± 0.09) vol.%, CH₄ = 1.48 (± 0.01) vol.%, O₂ = 9987 (± 80) ppmv, H₂S = 83 (± 5) ppmv, COS = 6.55 (± 0.11) ppmv.

3.1.4. The composition of the producer gas from gasification of straw and RDF pellets

The same experimental procedures were repeated, this time using various compositions of the producer gas from gasification of straw and RDF pellets. The average values of concentration of components are presented in Table 3.

As can be seen in Table 3, there are obvious differences in the composition of the gas streams generated by gasification of different biomass sources. The straw pellets produce a slightly higher H₂S gas concentration, and the COS concentration is very similar. According to Little [16], the typical sulphur content in straw pellets was about 0.1 wt.%, which was higher than those of wood pellets made from heather (0.07 wt.%), gorse (0.08 wt.%), and rhododendron (0.02 wt.%).

416 The concentration of H₂S and COS produced from RDF pellets is about three
417 times higher than values from the wood and straw pellets. This is not surprising, as the
418 RDF was expected to have higher sulphur content. Depending on the source of RDF, its
419 sulphur content will vary. As an example, based on information from one supplier [17],
420 sulphur levels generally vary from 0.12 to 0.17 wt.%, yet can even be as low as 0.09
421 wt.%, or peak as high as 0.3 wt.%.

422 There is also consistency in the molar ratio of the concentration of H₂S to COS
423 (around 10:1) for gasification of wood, straw and RDF pellets, in which the temperature
424 in the hot zone was observed as high as 1084 °C. This information will also be very
425 useful when gas clean-up strategies need to be developed for commercial plants.

426 The results also show that there is a certain amount of O₂ in the gas stream, and
427 this can vary. This clearly depends on the design of the gasifier and operating
428 parameters. For example, the concentration of O₂ in the gas from the RDF pellets was
429 higher, because the pellets were large relative to the i.d. of the tube (higher void fraction
430 and wall channelling). The presence of O₂ in the producer gas streams is also reported in
431 the literature [18].

432 The concentration of the main components in the gas is also compared with
433 earlier experiments [15], using GC (with a TCD) for gas analysis. Although there are
434 slight differences, the comparison in general is very good. Slight differences probably
435 arise from slight variations in operating conditions/composition of pellets used.

436 Thus, it can be concluded that the developed QMS methodology had been
437 upgraded successfully to measure up to 8 species, including the main gases (N₂, H₂,
438 CO₂, CO, CH₄) and other trace gases (O₂, H₂S and COS). It was also shown that an
439 acceptable level of repeatability can be achieved. Also, provided that gas pre-cleaning

440 was effective, the mass spectrometer was stable for months without needing to be re-
441 calibrated.

442

443 ***3.2. Measurements on a pilot-scale plant***

444

445 ***3.2.1. The actual waste-wood processed***

446 Samples were taken of the waste-wood that was processed, and this is illustrated
447 in Figure 5. This clearly shows that the sample consists of wood from a variety of
448 different sources (e.g. bark, used wood, painted wood), and that it also contains small
449 quantities of cardboard, brown paper, and even plastics.

450 Samples of the waste-wood and waste-wood-derived char, were analyzed, and
451 their key properties (proximate analysis on a wt.% wet basis), are: moisture = 9.97;
452 volatiles = 70.57; fixed carbon = 19.13; ash = 0.33).

453

454 ***3.2.2. The composition of the gas produced from the pilot-plant***

455 **Initiation of reactions in the gasifier:** At the start of each run, reactions in the
456 gasifier are initiated by starting the blower, which draws air through the gasifier. An
457 ignited lance (through which propane flows) is then inserted into the throat of the
458 gasifier, which sustains a flame to initiate reactions in the gasifier. When temperatures
459 start to rise in the throat of the gasifier, and gas temperatures from the gasifier also rise,
460 the supply of propane is turned-off, and the lance is withdrawn.

461 By selecting the following key parameters: (a) temperatures at the top and
462 bottom of the throat (in the gasifier, but measured near the wall of the throat); (b)
463 producer gas flow; (c) producer gas composition (N₂, CO, CO₂, H₂, CH₄ and O₂); and

464 (d) the sulphur species, H_2S and COS , in the gas, the results of one test run are
465 summarized in Figure 6. In general, during this run, temperatures fluctuated at the top
466 and the bottom of the throat, and gas flow varied depending on the choice of operating
467 conditions.

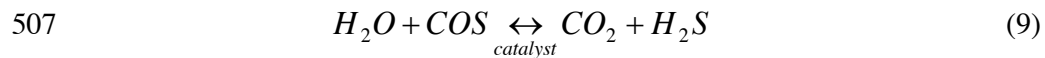
468 Looking at the data, the following general observations can be made:

- 469 ▪ As the blower speed was increased, the flow of air into the gasifier increased,
470 and temperatures in the gasifier increased. The flow of gas from the gasifier
471 also increased, as more gas was drawn by the centrifugal blower.
 - 472 ▪ As the unit was started-up, the composition of the gas changed (see Figure 6
473 (b)), providing a very clear indication of the point at which H_2 and CO
474 started to be produced, and O_2 was consumed.
 - 475 ▪ In general, as temperatures in the gasifier increase (above and below the
476 throat), the concentration of CO decreases (from 23 to 16 vol.%), whereas
477 that of H_2 increases (from 10 to 15 vol.%).
 - 478 ▪ At various fixed operating speeds of the blower, the gas composition
479 fluctuates (for example, see Figure 6 (b)), and this most probably arises from
480 the nature of the gasification process (and composition of waste-wood) that
481 is taking place in the throat of the gasifier. Although some gas back-mixing
482 will occur in the pipework and process units before the gas sampling point,
483 the fact that these fluctuations still remain indicates the presence of far
484 bigger variations in gas composition at the base of the actual gasifier.
- 485 However, considering the nature of the waste-wood feedstock, and the
486 variations in size of the feedstock (Figure 5), this is not surprising. For
487 example, for a fixed operating speed of the blower at 40 %, it is interesting

488 to see that these variations are approximately: CO = 16.0 (± 1.8) vol.%, H₂ =
489 11.9 (± 2.9) vol.%, CO₂ = 15.8 (± 1.4) vol.%, N₂ = 54.1 (± 3.3) vol.%, CH₄ =
490 1.9 (± 0.7) vol.%, O₂ = 0.3 (± 0.2) vol.%.

- 491 ▪ In Figure 6(c), the changes in H₂S and COS levels are shown. The
492 concentration of H₂S varies from about 200 to 700 ppmv. This is not
493 surprising as this will vary depending on the composition of the waste-wood
494 that is being gasified at a particular moment.
- 495 ▪ The COS concentrations were in the region of 6 to 17 ppmv, which are ~30
496 times smaller than the concentrations of H₂S. This is different from the
497 findings in the laboratory, where the molar ratio of H₂S:COS was around
498 10:1 for all three types of biomass (wood, straw and RDF pellets). This
499 difference might arise from the possibility of COS hydrolysis reactions
500 taking place in the water quench and HESS units with the presence of ash
501 particles as a catalyst - if it occurred, this would lead to the conversion of
502 COS into H₂S.

503 In a recent patent, McDaniel [19] reported a method and apparatus for
504 removing COS from a producer gas stream *via* wet scrubbing in the presence
505 of ash particles. The ash particles contained alumina oxide, which could
506 exhibit catalytic properties for the reaction.



508 McDaniel [19] found that if the producer gas stream from the gasifier went
509 directly into a wet scrubber (without passing through any other particulate
510 removal devices), then up to a 30 % drop in the COS occurred across the

511 scrubber. This depended on the design of the scrubber and its operating
512 conditions, and flooding conditions were preferred.

513

514 **4. Conclusions**

515

516 Using QMS, a quantitative method of on-line gas analysis was developed to
517 measure gas composition when a range of fuels was gasified. The method is informative
518 and the data provides an indication of gas composition, especially on the trace
519 components H₂S and COS for which there is relatively little data. From measurements
520 on a commercial scale down-draft pilot-scale gasifier (with waste wood as fuel),
521 valuable data was obtained during the start-up phase. In addition it was found that the
522 H₂S:CO ratios were higher than obtained in laboratory experiments, and this has
523 important implications for the choice of gas clean-up equipment to remove sulphur
524 compounds.

525

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531

532

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580

581 **Figure Captions**

582

583 **Figure 1.** Outline schematic of the gasification experiment, focusing on gas analysis.

584 **Figure 2.** Simplified process flow diagram of the commercial pilot-scale plant.

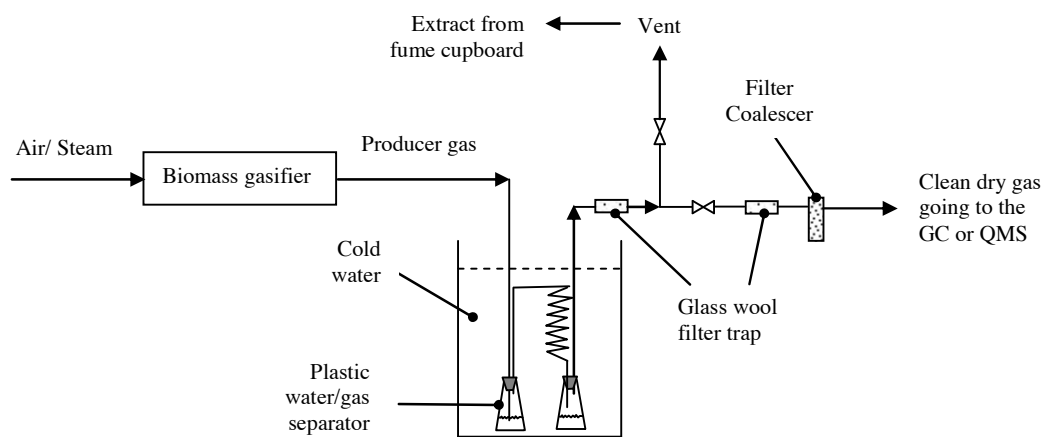
585 **Figure 3.** Comparison between QMS and GC measurements (data points correspond to
586 GC measurements).

587 **Figure 4.** Composition of dry gas from gasification of wood pellets: (a) main gases and
588 (b) trace gases.

589 **Figure 5.** Photograph of a sample of waste-wood used.

590 **Figure 6.** The results of a test run performed on the pilot-plant: (a) temperature and gas
591 flow, (b) dry gas composition, and (c) concentration of H₂S and COS in dry gas.

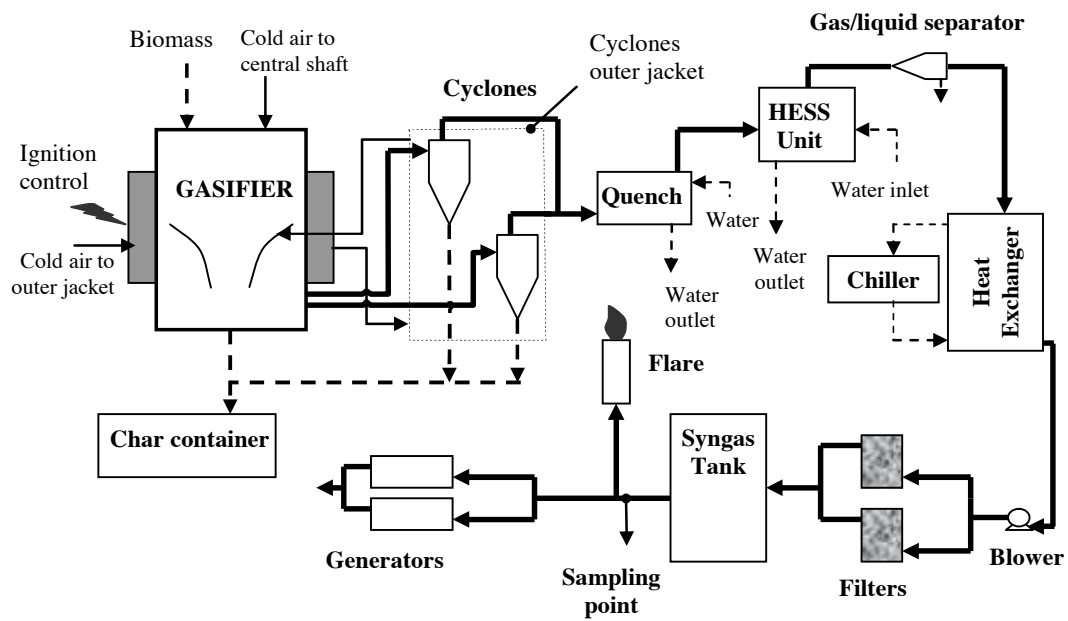
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594 **Figure 1**

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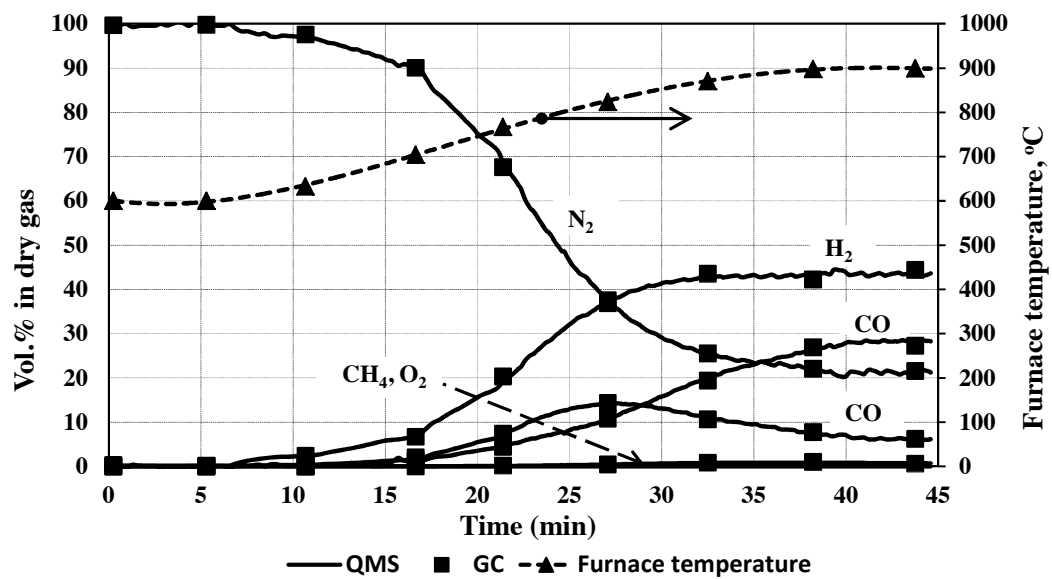


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597 **Figurer 2**

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600

601 **Figure 3**

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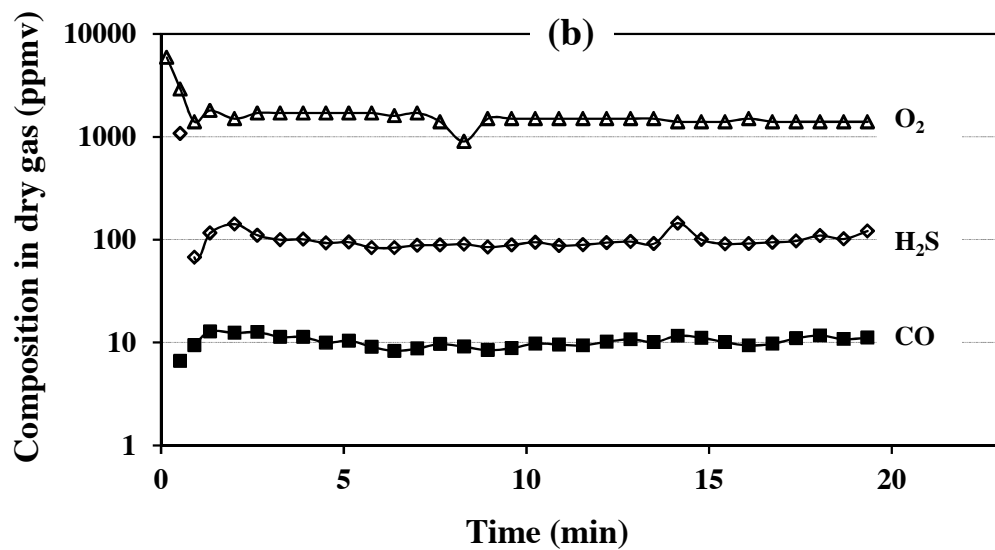
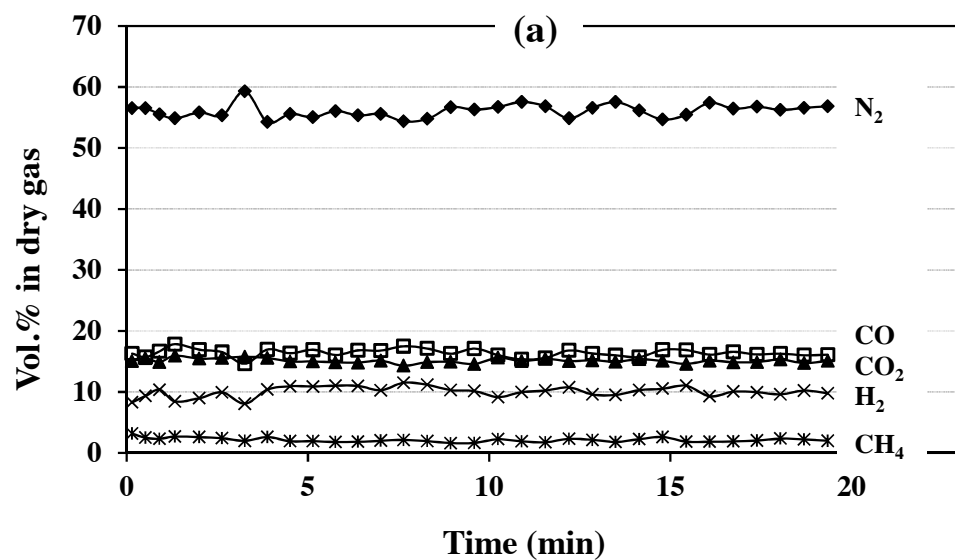


Figure 4



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Figure 5

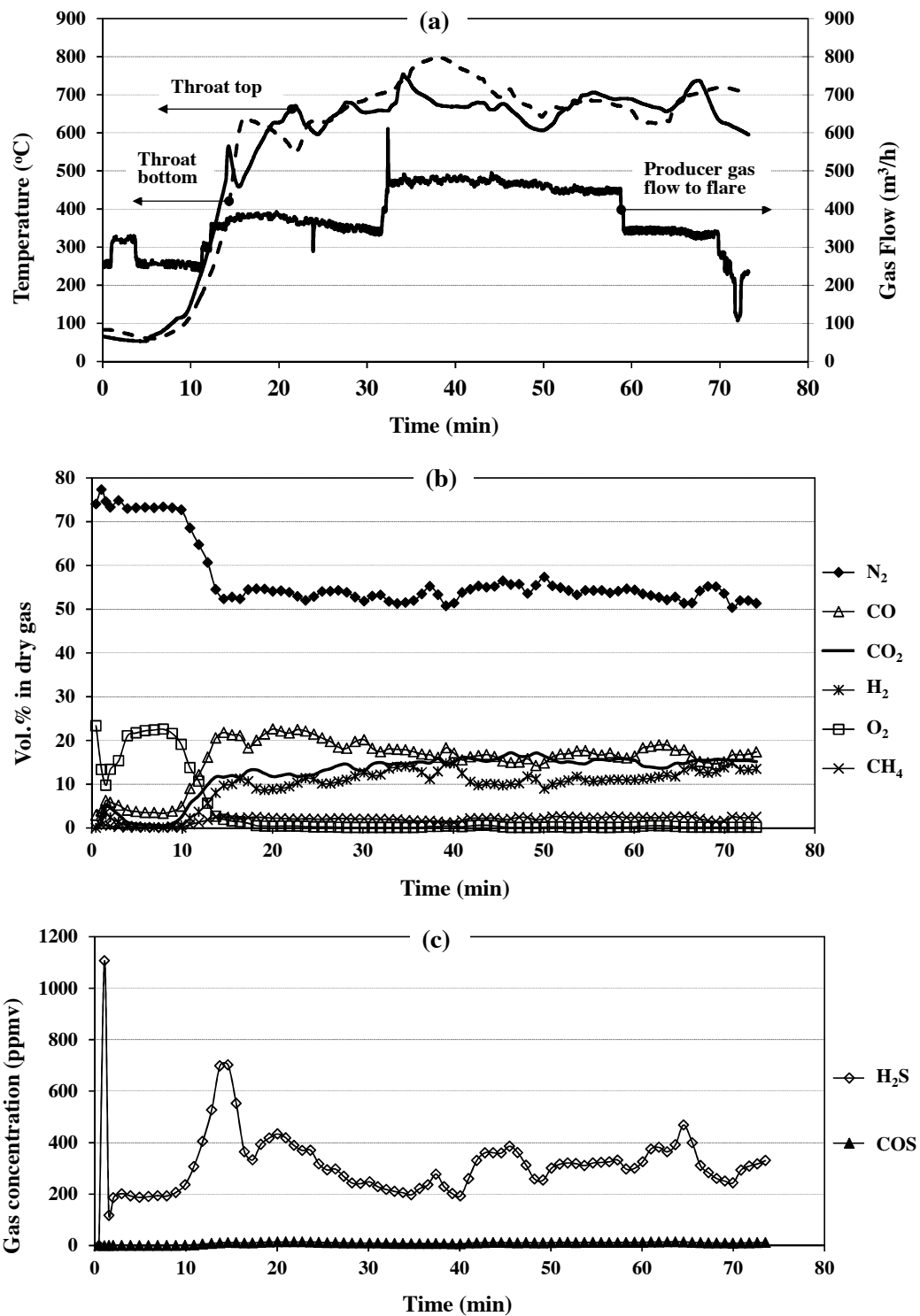


Figure 6

612 **Table 1.** Analysis matrix for the gas produced from biomass gasification.

Component	Mass							
	2	14	15	28	32	34	44	60
H₂	x							
CH₄		x	x					
CO₂				x			x	
N₂		x		x				
CO		x		x				
O₂					x	x		
H₂S					x	x		
COS								x

613

614

615 **Table 2.** Properties of the fuels used with proximate analysis.

Properties	Wood Charcoal ⁽¹⁾	Wood pellets ⁽²⁾	Straw pellets ⁽³⁾	RDF pellets ⁽⁴⁾
Dimensions:				
Diameter, mm	4	5	6	14
Length, mm	4	5 - 17	5 - 17	30 - 80
Moisture (wt.% in wet basic)	4.7	7.4	10.9	7.2
Volatiles (wt.% in wet basic)	11.3	72.6	65.9	39.7
Fixed carbon (wt.% in wet basic)	82.8	18.8	21.7	29.2
Ash (wt.% in wet basic)	1.2	1.3	1.4	23.9

616 ⁽¹⁾ Obtained from an actual pilot-plant that has used wood pellets as fuel.

617 ⁽²⁾ Supplied by Treenergy Ltd, Monmouth.

618 ⁽³⁾ Supplied by Agripellets Ltd, Evesham.

619 ⁽⁴⁾ Supplied by Refgas Ltd, Sandycroft.

620

621 **Table 3.** Comparison of gas compositions produced from different biomass sources.

Component	Previous study (Kolaczkowski <i>et al.</i> , 2011b), GC used for analysis		Current study, QMS used for analysis		
	Wood pellets	Straw pellets	Wood pellets	Straw pellets	RDF pellets
CO, vol.%	15.8	14.7	16.44	13.91	10.39
H ₂ , vol.%	9.5	12.6	10.11	12.83	4.97
CH ₄ , vol.%	2.0	2.0	2.08	2.11	1.11
CO ₂ , vol.%	14.5	14.2	15.12	17.17	14.57
N ₂ , vol.%	58.2	56.5	56.06	53.77	67.90
O ₂ , ppmv	-	-	1510	1736	10063
H ₂ S, ppmv	-	-	99	123	286
COS, ppmv	-	-	10	11	28

622

623

624